

LOCALIZED CORROSION OF FERRALIUM STAINLESS STEEL
IN PAPER MACHINE WHITE WATER

BY

N. N. Girgis and I. M. Ghayad

Central Metallurgical Research & Development Institute
(CMRDI). Helwan, Cairo, (Egypt)

Received: 25-3- 1992

ABSTRACT

The cyclic anodic polarization test was used as a method for predicting localized corrosion resistance of stainless steels in synthetic paper machine white water constituents. Ferralium demonstrated a considerably superior resistance to localized corrosion to that of 316L in chloride solutions. The effect of Cl^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , and S^{2-} anions, individually or in combination with each other, on localized corrosion resistance of Ferralium at pH 4 and 50 C has been investigated. Thiosulfate with chloride, sulfate or sulfide are the most aggressive solutions. Sulfate alone or sulfate and chloride mixture solution containing high concentrations (1000 ppm for each) are the least aggressive. Chloride is midway within the two ends of the scale. The role of each anion in enhancing or suppressing local attack has also been discussed.

INTRODUCTION

Paper machine white water is derived from fiber, papermaking additives, and raw water. So the final chemical

Delta J. Sci. 16 (1) 1992

Localized Corrosion

composition of the white water is unique each individual mill regardless of category and/or paper product. In general, white water closure affects corrosivity by a substantial increase of dissolved solids, temperature, and biological activity. Both organic and inorganic constituents in the dissolved solids influence the severity of corrosion and most significant among these are chlorides, sulfates, thiosulfates, sulfites, sulfides, alum, lignin-related sulfur compounds, organic acids, and carbonates. The corrosion of metals by paper machine white water may be uniform and/or localized. Surveys (1-27) are underway to characterize the chemistry of various white water systems, define a relative measure of its corrosivity, and determine the present status of white water closure with the industry.

The present work was undertaken to compare the corrosive effect of various anions, individually or in combination with each other, roughly corresponding to the combination present in the white water environment. The test metal was Ferralium although stainless steel 316 L was used in a limited number of experiments.

EXPERIMENTAL

Disc specimens (15.0 mm diameter and 2 mm thickness) of 316L and Ferralium stainless steels, whose chemical compositions are given in Table 1, were used. Before testing, each specimen was ground, cleaned, degreased, dried then mounted in a specimen holder, to expose 1 cm^2 surface area.

Delta J. Sci. 16 (1) 1992

Girgis and Ghayad

Five neck flask was used as a corrosion cell in which metal specimen represents the working electrode. Two graphite counter electrodes and a saturated calomel electrode (SCE) were used. Temperature was controlled by ultrathermostat. Cyclic anodic polarization curves (4,13,15), a suitable method for studying localized corrosion, were measured by using a Wenking Potentiostan (POS 73), under aerated condition. Beginning with one hour hold in test solution, at open circuit, then scanning at a rate of 0.2 mV/S to an anodic potential. Potential scan reversal was commenced at an applied current density of approximately $1000 \mu\text{A}/\text{cm}^2$.

In an attempt to study the corrosive nature of each of white water constituents, the test cell environments were solutions of bidistilled water plus concerned chemical(s): NaCl, Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , Na_2S , HCl, H_2SO_4 and NaOH. The pH adjustments involved additions of less than 50 ppm acid anion (Cl^- or SO_4^{2-}) and these were taken into account in the calculated adjusted anion values. The concentrations were, within the range, based on the reported compositions given previously, but the level of some constituents like Cl^- , $\text{S}_2\text{O}_3^{2-}$, ... etc were intentionally increased to simulate salt build-up inclosed systems.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic polarization curves for 316L and Ferralium stainless steels in chloride solutions. Table 2 gives the corrosion parameter values; E_{corr} , E_b , E_p ,

Delta J. Sci. 16 (1) 1992

Localized Corrosion

$(E_b - E_{corr})$, and $(E_p - E_{corr})$; deduced from such polarization curves; for selected alloys and varying environmental conditions. It can be noticed that Ferralium shows better localized corrosion resistance over 316L in chloride solutions; where E_b , E_p , $(E_b - E_{corr})$ and $(E_p - E_{corr})$ values are much higher. On the other hand an increase in chloride content (from 500 ppm to 1000 ppm) reduces pitting resistance of 316 L whereas the effect is not pronounced for Ferralium. Also, as the pH increases (from 3 to 5) pitting resistance of Ferralium is increased; the E_b shifts linearly in the noble direction (50 mV/pH).

The effect of sulfate or thiosulfate anion on cyclic anodic polarization curve for Ferralium is shown in Fig. 2. It is clear that 1000 ppm chloride is more aggressive than 1000 ppm thiosulfate, which in turn is more aggressive than 1000 ppm sulfate. Table 3 shows that increasing sulfate ion levels has no effect on the different parameters E_b , E_p , $(E_b - E_{corr})$ or $(E_p - E_{corr})$; E_b is markedly noble than for Cl^- or $S_2O_3^{2-}$ indicating that Ferralium shows high pitting corrosion resistance. It is interesting to note that in the case of thiosulfate the localized attack passes through a maximum at 500 ppm.

Figures 3,4 and 5, as well as Table 4, illustrate the results obtained for Ferralium in Cl^-/SO_4^{2-} , $Cl^-/S_2O_3^{2-}$, and $SO_4^{2-} / S_2O_3^{2-}$ solution mixtures respectively. It is interesting to note that pitting resistance increases in the order

Delta J. Sci. 16 (1) 1992

Girgis and Ghayad

$1000 \text{Cl}^- / 500 \text{SO}_4^{2-} < 500 \text{Cl}^- / 1000 \text{SO}_4^{2-} < 1000 \text{Cl}^- / 1000 \text{SO}_4^{2-}$,
for the first set and $1000 \text{Cl}^- / 500 \text{S}_2\text{O}_3^{2-} < 500 \text{Cl}^- / 1000 \text{S}_2\text{O}_3^{2-} <$
 $1000 \text{Cl}^- / 1000 \text{S}_2\text{O}_3^{2-}$ for the second. For the third set, however,
the resistance does not depend on the ionic ratios in the
three mixtures:

$1000 \text{SO}_4^{2-} / 500 \text{S}_2\text{O}_3^{2-}$, $500 \text{SO}_4^{2-} / 1000 \text{S}_2\text{O}_3^{2-}$ or $1000 \text{SO}_4^{2-} / 1000 \text{S}_2\text{O}_3^{2-}$

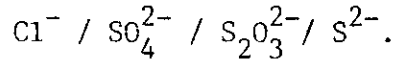
It is worth mentioning that sulfate inhibits the action of chlorine when its concentration is 1000 ppm. But if reduced to 500 ppm the pitting potential is markedly shifted in the negative direction. So sulfate ion concentration is the limiting factor in chloride/ sulfate mixtures.

On the other hand, 1000 ppm $\text{Cl}^- / 500 \text{ppm S}_2\text{O}_3^{2-}$ mixture is the most aggressive chloride/ thiosulfate mixtures. The other two chloride / thiosulfate mixtures, which are nearly the same in the level of aggressiveness, contain the same thiosulfate content (1000 ppm). Since 500 ppm $\text{S}_2\text{O}_3^{2-}$ is more aggressive than 1000, it follows that thiosulfate ion is also the determining factor in chloride/ thiosulfate mixtures. For sulfate / thiosulfate mixtures, 1000 ppm SO_4^{2-} is enough to inhibit local attack in presence of 500 ppm $\text{S}_2\text{O}_3^{2-}$. Furthermore 500 ppm SO_4^{2-} can inhibit 1000 ppm $\text{S}_2\text{O}_3^{2-}$.

To investigate the role played by Na_2SO_3 or Na_2S , other tests had been conducted and results are shown in Fig. 6 and Tables 5. It can be stated that pitting resistance decreases in the order: $\text{Cl}^- / \text{SO}_4^{2-} / \text{S}_2\text{O}_3^{2-} > \text{Cl}^- / \text{SO}_4^{2-} / \text{S}_2\text{O}_3^{2-} / \text{SO}_3^{2-} >$

Delta J. Sci. 16 (1) 1992

Localized Corrosion



It is shown that the addition of sulfide ions causes severe local attack. Moreover, corrosion in sulfide environment obeys an active-passive transition behaviour with pronouncedly higher passive current density.

Taking the breakdown potential, E_b , as a characteristic parameter for aggressiveness of different, single ions or mixtures of these ions we may have the order shown in Table 6. It can be stated that sulfate alone or sulfate and chloride mixtures, containing high concentrations (1000 ppm for each), are least aggressive. On the other hand the most aggressive solutions are those of thiosulfate with chloride, sulfate or sulfide. This high aggressiveness is slightly decreased when thiosulfate is alone or when we have chloride and sulfate (1000 to 500 ppm). It is also of interest to note that chloride assumes midway values on the scale, i.e., chloride is moderate as compared to thiosulfate alone or in mixture and is inhibited by equal amounts of sulfate. However, high concentrations, of the three ions lead to passivation; which may be due to blocking the metal surface.

One of the major influences of chloride ion is that, the metal chlorides are so soluble that a sharp increase in H^+ activity can occur as the dissolved metal ion concentration increases [24]. This in turn causes a sharp increase in

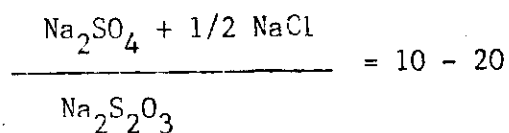
Delta J. Sci. 16 (1) 1992

Girgis and Ghayad

the critical current density for passivation in the pit solution, eventually eliminating passivity altogether.

It is well established that stainless steels do not pit in pure sulfate solutions. The reason is that the hydrolysis of chromium ions cannot lower the pH to a sufficiently low value to sustain the very high dissolution rate required for pit initiation [23].

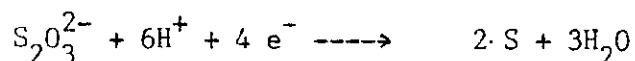
Thiosulfate is an aggressive pitting agent [12], especially for stainless steels that do not contain Mo. Unlike chloride pitting, thiosulfate pitting occurs below a certain critical potential- the thiosulfate reduction potential-which is usually below E_b [12]. Reduction of thiosulfate in the presence of hydrogen ions produces an adsorbed sulfur monolayer on the metal surface. The adsorbed sulfur activates the anodic dissolution of the metal and hinders repassivation. Excess hydrogen ions must be present for acidification of the pit; further there must also be a larger amount of inert ions (sulfate and / or chloride) that can be transported into the pit to meet charge transfer requirements. The worst condition for thiosulfate pitting occurs at a certain thiosulfate concentration (500 ppm) in the case of single solutions; or within the molar concentration ratio [12]:



Delta J. Sci. 16 (1) 1992

Localized Corrosion

in the case of mixed ions solutions. Above the range represented by the ratio (or below this certain value) there is insufficient thiosulfate ions to reach the pit nucleus. Below this range (above this certain value) there is too much thiosulfate reduction, which prevents acidification of the pit according to reaction such as:



and probably preventing chloride accumulation in chloride/thiosulfate solution.

However, once the pit is formed [12], through the reduction of thiosulfate, it is very stable and are not subject to spontaneous repassivation; and may be stabilized by chloride or sulfate ions. In addition, ferrous thiosulfate is highly soluble [20].

The aggressive nature of sulfide could be demonstrated by deliberately adding sulfide ions to our mixtures, thus intensifying the action of those produced through the reduction of the thiosulfate ions. Furthermore, formation of porous sulfide deposits probably has important effects in retaining pit contents and promoting pitting in sulfur containing electrolytes.

CONCLUSIONS

1- In chloride solutions, Ferralium is more resistant than 316L SS and the local attack on the former decreases linearly with increase in pH.

Delta J. Sci. 16 (1) 1992

Girgis and Ghayad

- 2- At a certain concentration (500 ppm), thiosulfate ion is more aggressive than chloride ion.
- 3- Pitting resistance of Ferralium in $\text{Cl}^- / \text{SO}_4^{2-}$ or $\text{Cl}^- / \text{S}_2\text{O}_3^{2-}$ mixture decreases as Cl^- to SO_4^{2-} or $\text{S}_2\text{O}_3^{2-}$ ratio tends to two. Sulfate or thiosulfate ion concentration is the limiting factor in such corresponding chloride mixtures.
- 4- Ferralium is pitted by Na_2S and to lesser extent by Na_2SO_3 . Non protective sulfide corrosion product is responsible for promoting pitting in sulfur-containing electrolytes.
- 5- Sulfate alone or sulfate and chloride mixture (1000 ppm/1000 ppm) are the least aggressive solutions; whereas thio-sulfate with chloride, sulfate or sulfide mixtures are the most aggressive ones; chloride occupies midway on such scale.

DeltaJ. Sci. 16 (1) 1992

Table 1 : Chemical composition of alloys, wt %

Alloy	Structure	Cr	Ni	Mn	C	N	Si	P	S	Mo	Fe
316L	Austenitic SS	16	13	1.6	0.03	---	0.1	0.021	0.012	2.8	bal
Ferralium 255	Duplex SS	25	5	0.7	0.03	0.16	0.3	0.021	0.002	4.16	bal

Table 2 : Localized corrosion parameters of stainless steels in chloride-containing solutions at different pH values and 50 C

Alloy	Anion	C.ppm	pH	E_{corr} mV(SCE)	E_b mV(SCE)	E_p mV(SCE)	$(E_b - E_{corr})$ mV	$(E_p - E_{corr})$ mV
316L	Cl ⁻	500	4.0	131	150	-251	19	-382
		1000	4.0	38	-40	-93	162	-131
Ferralium		500	4.0	78	580	5	502	-73
		1000	4.0	94	550	34	456	-60
Ferralium		1000	3.0	186	490	-55	304	-241
Ferralium		1000	5.0	155	600	21	445	-134

where : c is the concentration in ppm

E_{corr} is the corrosion potential

E_b is the breakdown potential (pitting potential)

E_p is the protection potential

Table 3 : Localized corrosion parameters of Ferralium in different
one- constituent solutions at pH 4.0 and 50 °C

Anion	C, ppm	E_{corr} mV(SCE)	E_b mV(SCE)	E_p mV(SCE)	$(E_b - E_{corr})$ mV	$(E_p - E_{corr})$ mV
SO_4^{2-}	500	175	900	712	725	537
	1000	143	900	694	757	511
$S_2O_3^{2-}$	250	116	425	500	309	384
	500	135	290	450	155	315
	1000	166	550	650	384	484

Table 4 : Localized corrosion parameters of Ferralium in different
two- constituents solutions at pH 4.0 and 50 °C

Anion	C, ppm	E_{corr} mV(SCE)	E_b mV(SCE)	E_p mV(SCE)	$(E_b - E_{corr})$ mV	$(E_p - E_{corr})$ mV
Cl^- / SO_4^{2-}	1000/1000	207	1000	11	793	-196
	500/1000	212	900	630	688	418
	1000/ 500	192	350	-73	158	-265
$Cl^- / S_2O_3^{2-}$	1000/1000	115	200	495	85	380
	500/1000	182	340	536	158	354
	1000/ 500	179	250	-50	71	-229
$SO_4^{2-} / S_2O_3^{2-}$	1000/1000	170	200	506	30	336
	500/1000	207	200	617	-7	410
	1000/ 500	191	200	661	9	470

Table 5 : Localized corrosion parameters of Ferralium in different three and more than three constituents solutions at pH 4.0 and 50 °C

Anion	C, ppm	E_{corr} mV(SCE)	E_b mV(SCE)	E_p mV(SCE)	$(E_b - E_{corr})$ mV	$(E_p - E_{corr})$ mV
$Cl^- / SO_4^{2-} / S_2O_3^{2-}$	1000/1000/1000	155	800	645	645	490
$Cl^- / SO_4^{2-} / S_2O_3^{2-} / SO_3^{2-}$	1000/1000/1000/1000	244	350	222	106	-22
$Cl^- / SO_4^{2-} / S_2O_3^{2-} / S^{2-}$	1000/1000/1000/1000	245	220	-209	-25	-454

Table 6 : Aggressiveness of different, single or mixture, solutions to pitting for Ferralium at pH 4 and 50 C.

Breakdown Potential E_b , mV(SCE)	Aggressiveness to pitting	Environment
200 - 250		$S_2O_3^{2-} + Cl^-$ or $+ SO_4^{2-}$ or $+ S^{2-}$
290 - 400		$S_2O_3^{2-}$ alone or (500 SO_4^{2-} / 1000 Cl^-)
500		Cl^- alone
800		Mixture of $S_2O_3^{2-} + Cl^- + SO_4^{2-}$ (1000 each)
900 - 1000		SO_4^{2-} alone or (1000 SO_4^{2-} / 1000 or 500 Cl^-)

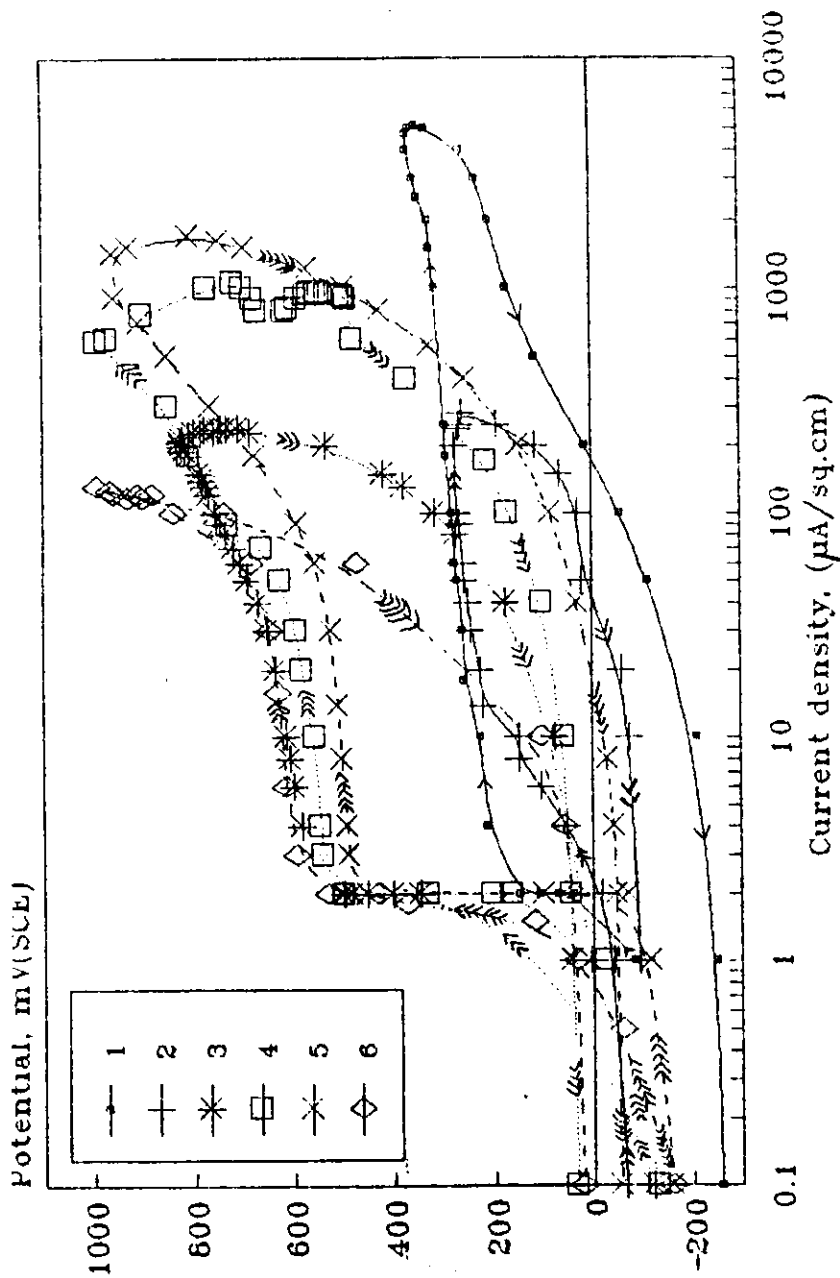


Fig. 1 : Cyclic anodic polarization curves for 316L and Ferralium stainless steels in chloride solutions at 50 C.

- 1 316L/500ppm Cl/pH 4
- 2 316L/1000ppm Cl/pH 4
- 3 Ferralium /500ppm Cl/pH 4
- 4 Ferralium/1000ppm Cl/pH 4
- 5 Ferralium/1000ppm Cl/pH 5
- 6 Ferralium/1000ppm Cl/pH 5

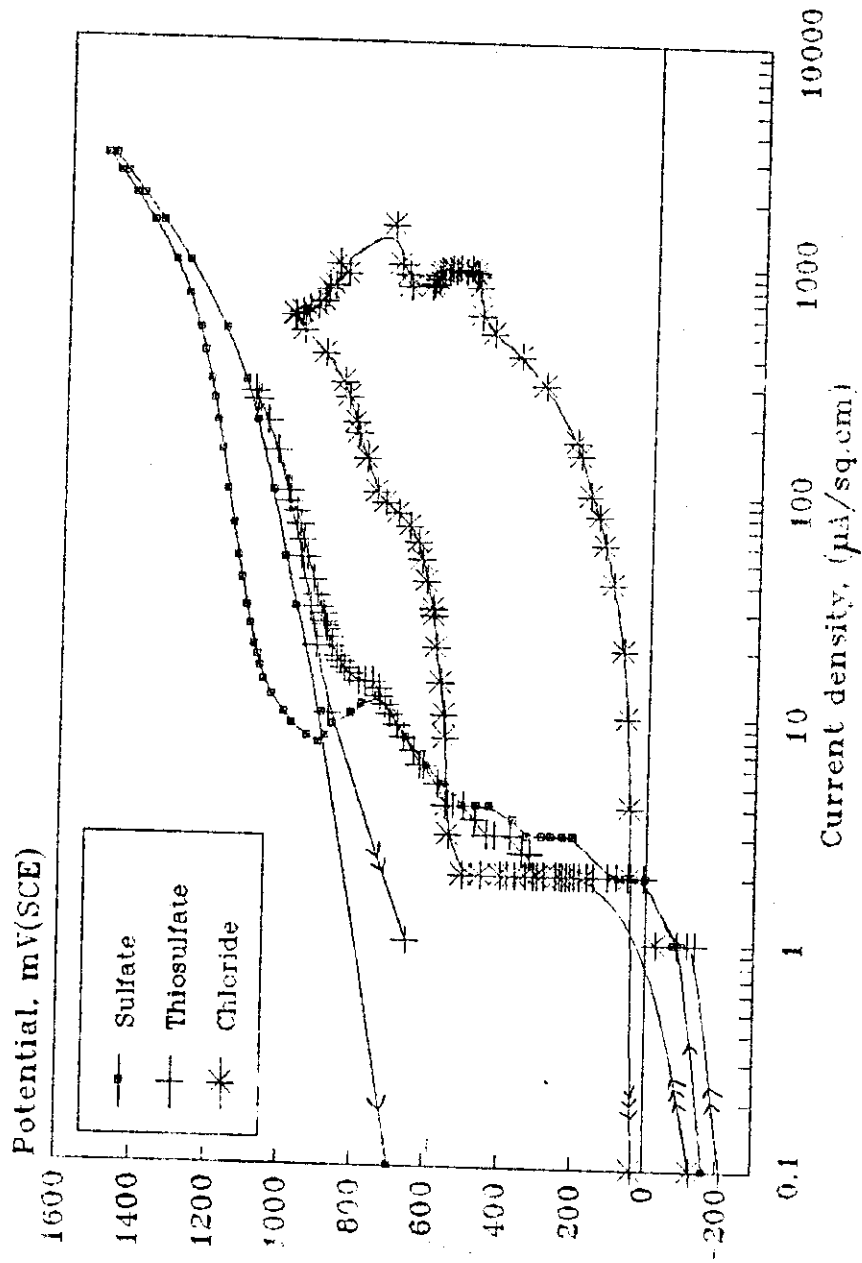


Fig. 2 : Effect of sulfate or thiosulfate anion on cyclic anodic polarization curve for Ferratum at pH 4 , 50 C and 1000ppm concentration. (chloride curve is given for comparison).

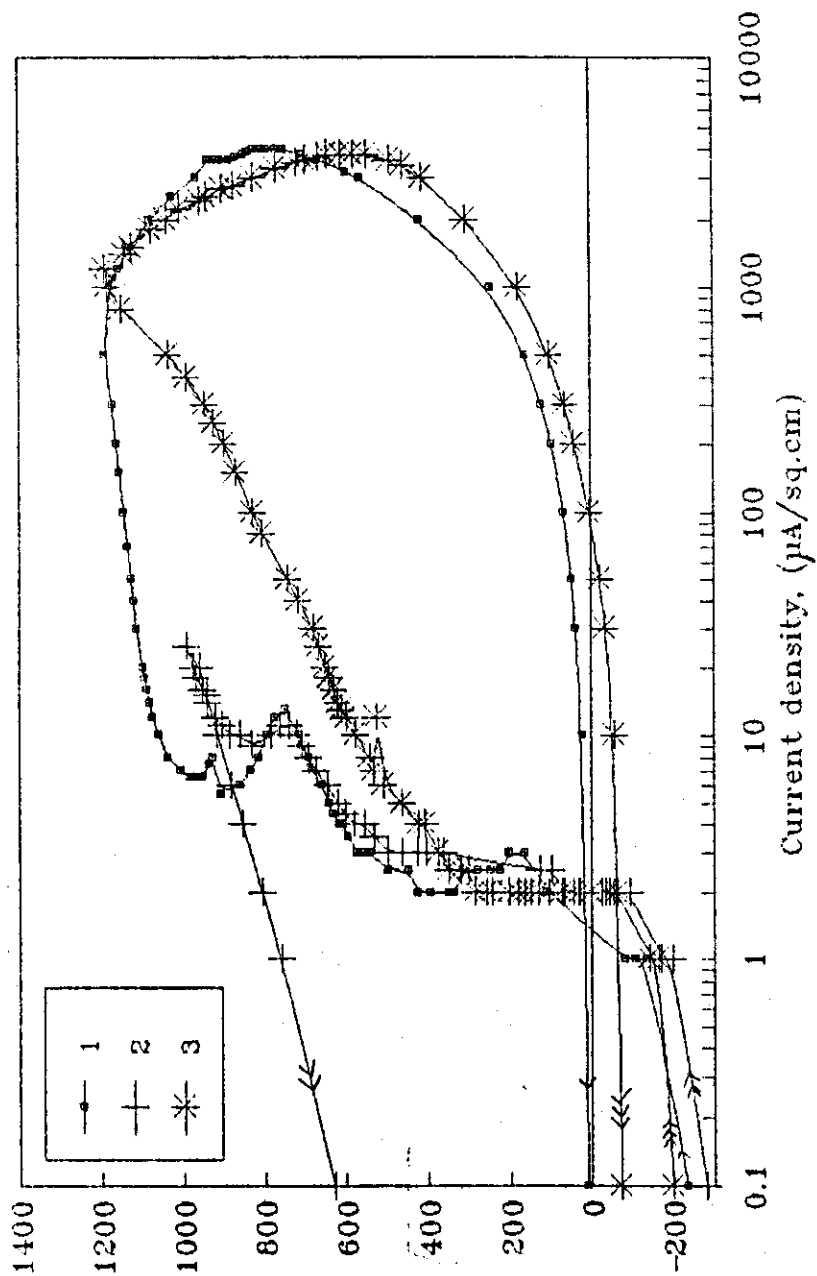


Fig. 3 : Cyclic anodic polarization curves for Ferratum in chloride-sulfate solutions at pH 4 and 50 C.
 1- 1000ppm chloride ion/1000ppm sulfate ion
 2- 500ppm chloride ion/1000ppm sulfate ion
 3- 1000ppm chloride ion/500ppm sulfate ion

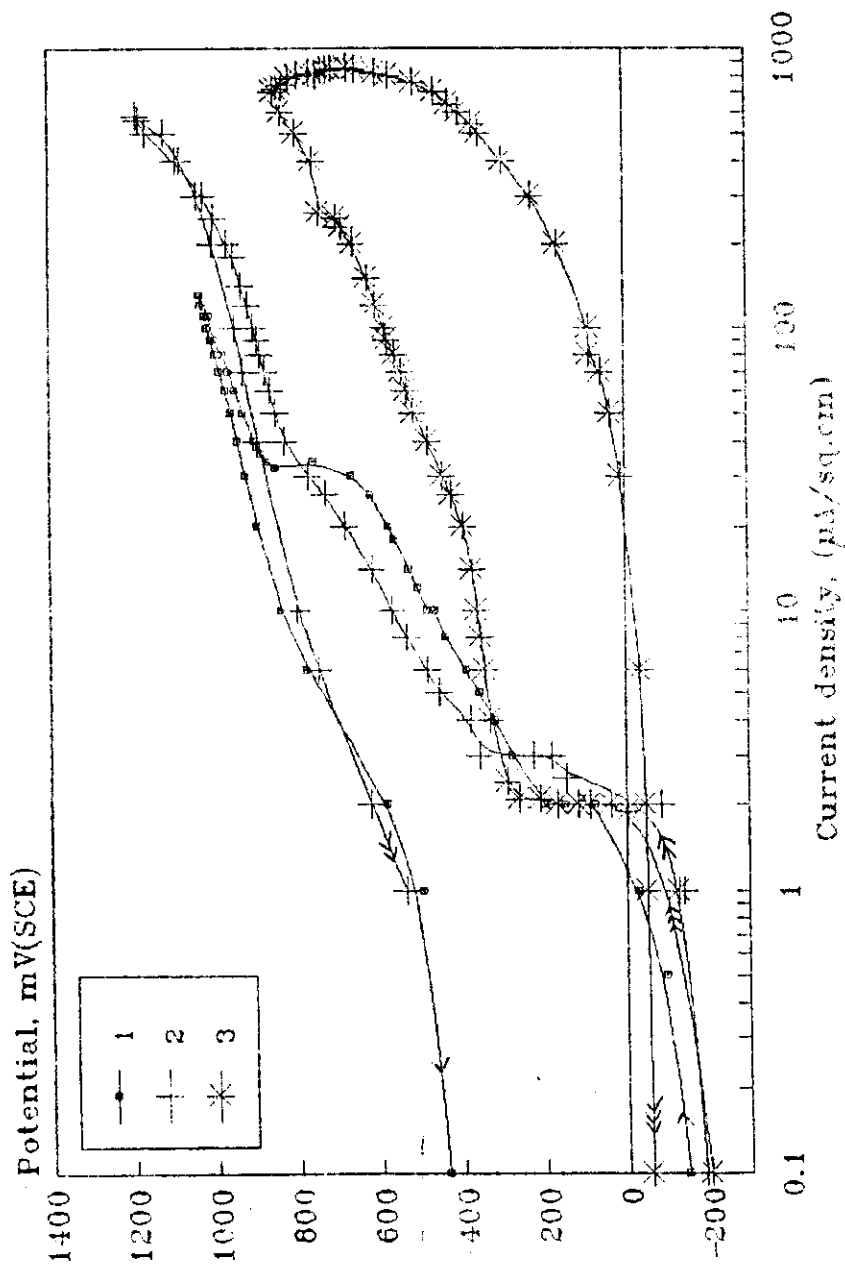


Fig. 4 : Cyclic anodic polarization curves for Ferralium in chloride-thiosulfate solutions at pH 4 and 50 C.

- 1- 1000ppm chloride ion/1000ppm thiosulfate ion
- 2- 500ppm chloride ion/1000ppm thiosulfate ion
- 3- 1000ppm chloride ion/500ppm thiosulfate ion

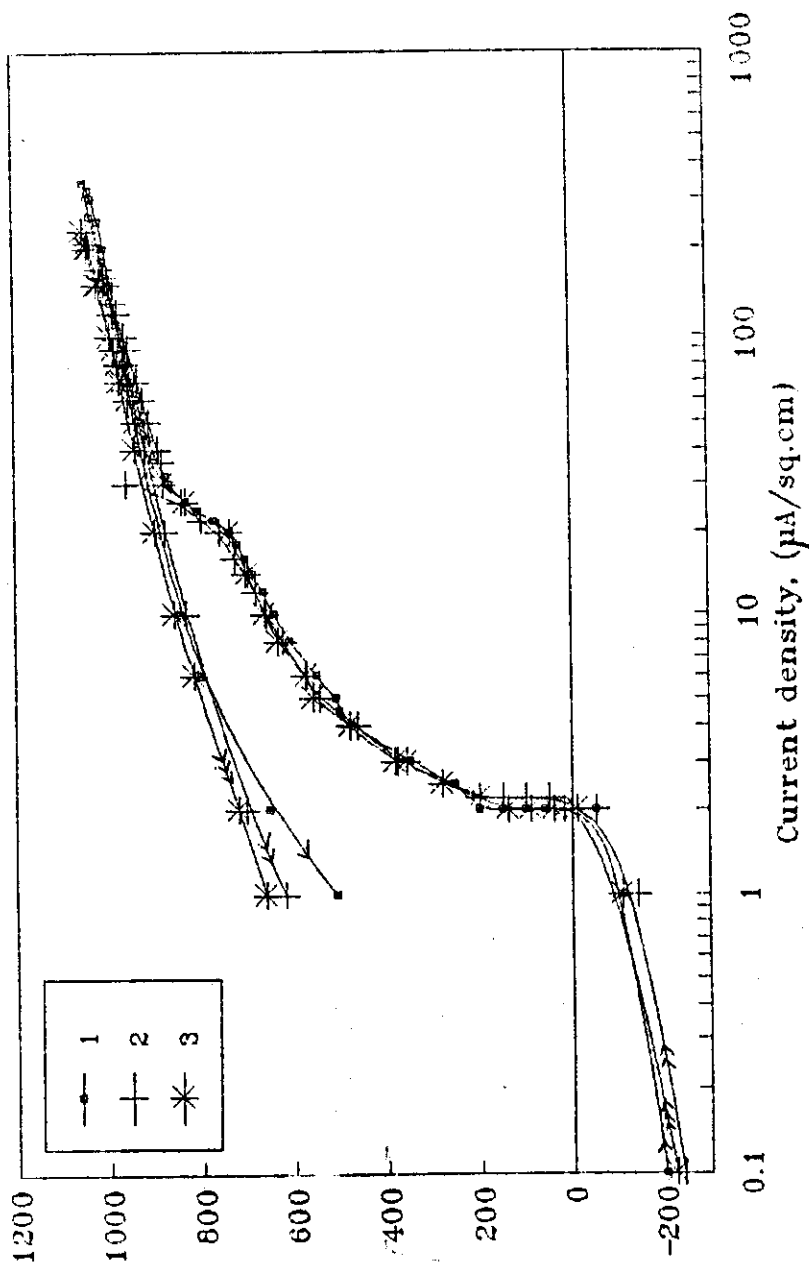


Fig. 5 : Cyclic anodic polarization curves for Ferralium in sulfate-thiosulfate solutions at pH 4 and 50 C.

- 1- 1000ppm sulfate ion/1000ppm thiosulfate ion
- 2- 500ppm sulfate ion/1000ppm thiosulfate ion
- 3- 1000ppm sulfate ion/500ppm thiosulfate ion

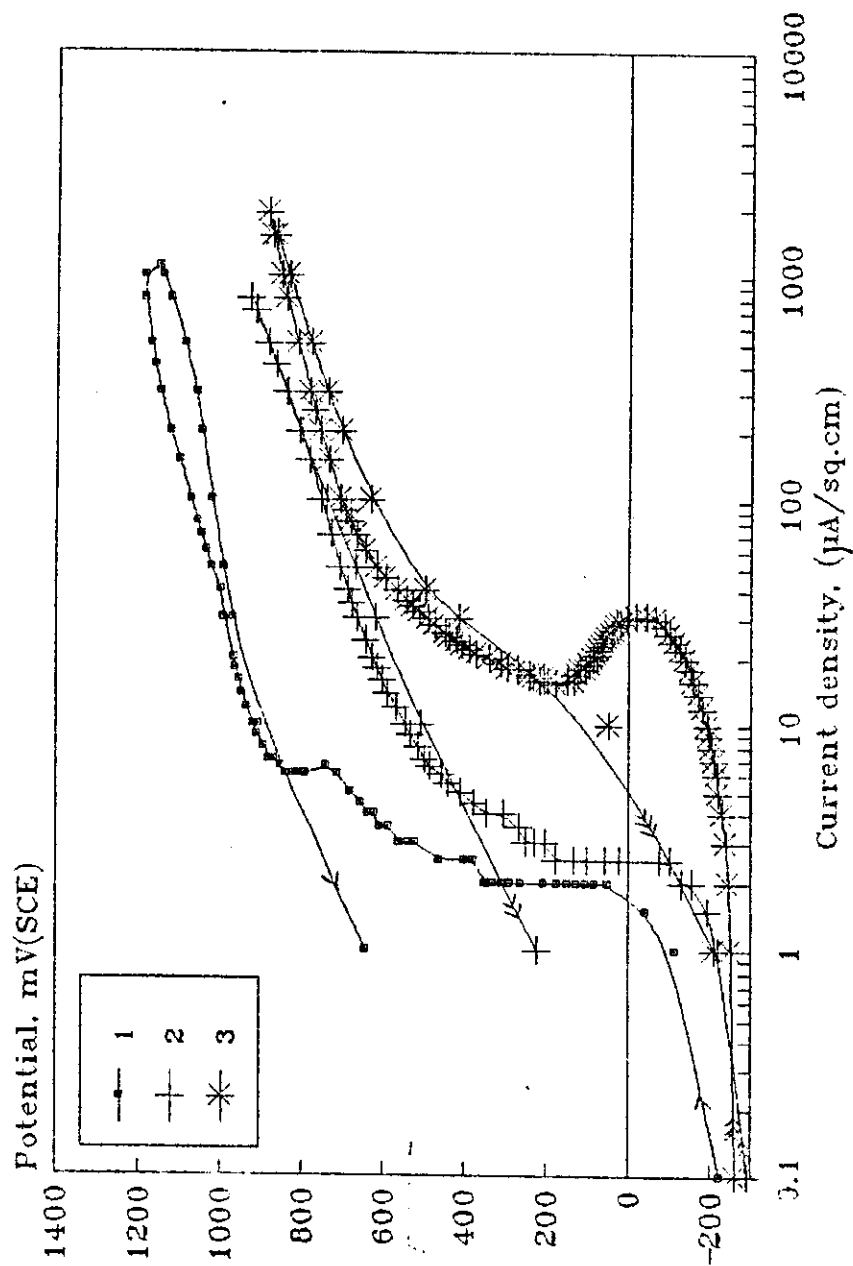


Fig. 6 : Effect of sodium sulfite or sodium sulfide on cyclic anodic polarization curves for Ferratum at pH 4, 50 C and 1000ppm anion concentrations.

- 1- chloride/sulfate/thiosulfate
- 2- chloride/sulfate/thiosulfate/sulfite
- 3- chloride/sulfate/thiosulfate/sulfide

Delta J. Sci. 16 (1) 1992

REFERENCES

- 1- Bowers, D.F., Tappi J 60 (No.10), 1977, P.57
- 2- Nathan, C.C., and Peluso, A.J., "Wet End Corrosion Problems in Paper Mills", Pulp and Paper Industry Corrosion Problems, Vol.2,p.126,NACE, Houston, Texas, 1977.
- 3- Sailes, V.,"Critical Components of the Paper Machine: Damage Caused by Metallic Corrosion", Pulp and Paper Industry Corrosion Problems, Vol. 2, p. 100, NACE, Houston, Texas, 1977.
- 4- Bennett, D.C., and Federowicz, C.J., Materials Performance, 21 (No. 4) 1982,p. 39.
- 5- Garner, A., Corrosion, 41 (No. 10) 1985, p. 587.
- 6- Bowers, D.F., Tappi J. 61 (No. 3), 1978, p.57.
- 7- Newman, R.C., Isaacs, H.S., and Alman, B., Corrosion, 38 (No.5), 1982, p.261.
- 8- Newman, R.C., Corrosion, 41 (No. 8), 1985,p.451.
- 9- Tromans, D., and Frederick, L., Corrosion, 40 (No.12), 1984, p. 633.
- 10- Tuthill, A.H., Rushton, J.D., Geisler, J.J., Heasley, R.,H., and Edwards, L., Tappi J., 62 (No.11), 1979 p. 49.
- 11- Mueller, W.A., and Muhonen, J.M., Tappi J., 55 (No. 4), 1972, p. 589.
- 12- Metals Handbook, 9th ed., American Society for Metals, Vol. 13, 1987, p. 1190.

Delta J. Sci. 16 (1) 1992

- 13- Laliberte, L.H., Mueller, W.A. Current Density Contour Maps: An Investigation of pitting and Crevice Corrosion. NACE National Conference, 1976, Houston, unpublished paper No. 105.
- 14- Syrett, B.C. Application of Electrochemical Techniques to study Corrosion of Metallic Implant Materials. NACE National Conference, 1976, Houston, Unpublished paper No. 116.
- 15- Efird, K.D., Moller, G.E. Materials Performance, 18 (No. 7), 1979, p. 39.
- 16- Garner, A., Pulp Paper Mag. Canada, 83 (No. 10) 1982, p. 20.
- 17- Garner, A., J. Pulp Paper Sci., 10 (No. 5) 1984, p. j51.
- 18- Newman, R.C., Sieradzki, K., Corros. Sci., 25, 1983, p. 363.
- 19- Newman, R.C., Sieradzki, K., Isaacs, H.S. Metall. Trans., 13A, 1982, P. 2015.
- 20- Isaacs, H.S. and Newman, R.C., Proc. Uhlig, H.H. 75th Birthday Symposium, Denver, 1981, p. 120. The Electro-chemical Society (1981).
- 21- Bowers, D.F., "Corrosivity of Paper Machine White Water Toward Stainless steels-Alum Acid Versus Alkaline Papermaking", Corrosion/ 83, paper No. 202, National Association of Corrosion Engineers (NACE), Houston, Texas, 1983.
- 22- Newman, R.C., Franz, E.M., Corrosion, 40 (No. 7), 1984, p. 325.

Delta J. Sci. 16 (1) 1992

- 23- Newman, R.C., Corrosion, 41 (No. 8), 1985.
- 24- Mankowski, J., Szklarsks- Simialowska, Z., Corros. Sci.,
15, 1975, p. 493.
- 25- Newman, R.C., Corros. Sci., 25, 1985, p. 341.
- 26- Sury. P., Corros. Sci., 16, 1976, p. 879.
- 27- Knittel, D.R.; Maguire, M.A.; Bronson, A.; and Chen,
J.; Corrosion, 38 (No. 5), 1982.

التآكل الموضعى لصلب الفريليم الغير قابل للصدأ فى المياه البيضاء، لماكينات تصنيع الورق

نبيل نصيف جرجس ، ابراهيم محمد غياض
قسم التآكل - مركز بحوث وتطوير الفلزات - التين- حلوان

استخدم اختبار الاستقطاب المصعدى الدائرى كطريقة للتنبؤ بالتآكل الموضعى للصلب الغير قابل للصدأ فى المكونات المختلفة والمحضرة معمليا للمياه البيضاء، لماكينات تصنيع الورق. أظهر صلب الفريليم مقاومة عالية للتآكل الموضعى عن الصلب رقم ٣١٦ ال فى محاليل الكلوريدات. تمت دراسة تأثير كل من ايونات الكلوريد ، الكبريتات ، الشوكبريتات ، الكبريتيت والكبريتيد ، منفردة او متحدة مع بعضها ، على مقاومة التآكل الموضعى لصلب الفريليم عند درجة حرارة ٥٠°م وأس هيدروجينى قدره ٤ ، وكانت محاليل الشوكبريتات مع الكلوريد او الكبريتات او الكبريتيد الاكثر ضراوة من ناحية التآكل الموضعى. أما محاليل الكبريتات بمفردها أو الكبريتات والكلوريد ، التى تحتوى على ١٠٠٠ جزء فى المليون من كل فكانت أقلها ضراوة. واحتلت محاليل الكلوريدات منتصف الطريق بينهما فى السلسلة. وقد تم شرح دور كل أيون فى اسراع او ابطاء عملية التآكل الموضعى هذه.